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D-81925 München (DE)(54) **Catalyst and method for producing phenols.**

(57) A catalyst for producing phenols consists essentially of;
an iron oxide;
a nickel oxide;
at least one first oxide selected from the group consisting of a vanadium oxide and a molybdenum oxide;
and
at least one second oxide selected from the group consisting of an alkali metal oxide and an alkaline earth metal oxide.

The catalyst is used to produce phenols from benzoic acid or an alkyl benzoic acid.

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BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention relates to a catalyst for producing phenol or alkyl phenol and to a method for producing phenol or alkyl phenol by gas phase oxidation of benzoic acid or alkyl benzoic acid under the presence of the catalyst.

2. Description of the Related Art

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Various methods and catalysts are known to produce phenol by gas phase contact oxidation of benzoic acid.

For example, JP-A-57-11932 (the term JP-A- referred to hereinafter signifies unexamined Japanese patent publication) disclosed a catalyst containing at least one of a copper compound, a vanadium compound, a silver compound, a lithium compound, a sodium compound, and a magnesium compound,
15 and a method using the catalyst.

JP-B-59-20384 (the term JP-B- referred to hereinafter signifies examined Japanese patent publication) disclosed a method using a catalyst containing oxides of copper, zirconium, and alkali metal and being supported on α -alumina. JP-B-64-934 disclosed a method using an oxide catalyst containing a variety of
20 metallic elements: namely, molybdenum as the essential component, at least one of vanadium, niobium, and tantalum, and at least one of copper, silver, manganese, iron, cobalt, nickel, rhodium, palladium, and platinum, and at least one of thallium, an alkali metal, and an alkaline earth metal.

The inventors conducted extensive study on the catalyst for phenol production and on the method for producing phenol, and provided the catalysts to produce phenol by gas phase contact oxidation of benzoic
25 acid, which catalysts include the catalyst of a nickel compound supported on a metallic oxide such as titania, magnesia, and α -alumina (JP-A-4-5250), the catalyst containing an iron oxide and a nickel oxide (JP-A-4-330944), the catalyst containing an iron oxide, a nickel oxide, and an alkali earth metal compound (JP-A-4-330945), the catalyst containing an iron oxide, a nickel oxide, and an alkali metal compound (JP-A-4-104837), the catalyst containing an iron oxide, a nickel oxide, an alkali metal compound, and an alkaline
30 earth metal compound (JP-A-4-330946), and the catalyst containing a composite metallic oxide having a spinel crystal structure.

Furthermore, the inventors provided a catalyst to produce phenol by gas phase oxidation of toluene, which catalyst contains a vanadium oxide, an iron oxide, and a nickel oxide (JP-A-4-277029).

However, the catalyst disclosed in JP-A-57-11932 is insufficient in both activity and selectivity, and the
35 method for producing phenol using the catalyst gives the conversion of benzoic acid of 50.5% and the selectivity to phenol of 88.6% at the maximum. In addition, when an exothermic reaction such as oxidation of benzoic acid is carried out using a catalyst containing a copper compound, the catalyst bed likely induces hot spots which raises a problem of sintering of the catalyst and of significant degradation of the activity. The method for producing phenol disclosed in JP-B-59-20384 also shows an insufficient conversion
40 and selectivity giving the conversion of benzoic acid of 63.7% and the selectivity to phenol of 82.2% at the maximum. Furthermore, the method induces the yield of a large amount of by-products such as diphenyl oxide, which significantly degrades the catalyst activity. The method also has an industrial disadvantage of necessity of refining stage for produced phenol.

The method for producing phenol disclosed in JP-B-64-934 also gives the conversion of benzoic acid of
45 75% and the selectivity to phenol of 89% at the maximum, which values are insufficient for industrial application. The method also has a problem of catalyst degradation with time.

All the three of above described methods gives a low space time yield of phenol (production amount of phenol per unit catalyst volume per unit time) not higher than 100, so the productivity is poor, and the methods are inapplicable to industrial process.

50 Regarding the production of cresol from toluic acid, which was disclosed in JP-B-64-934, the catalyst activity and the selectivity are insufficient giving the conversion of 45% and selectivity to m-cresol of 81% for the reaction of p-toluic acid (4-methyl benzoic acid), and gives the conversion of 48% and the selectivity to m-cr sol of 79% for the reaction of o-toluic acid (2-methyl benzoic acid). M. Hronec, et al. pointed out a difficulty for obtaining a high yield of cr sol species in the reaction system using a catalyst containing Cu
55 owing to the unstable intermediate reaction products (Applied Catalysis, 69 (1991) pp201-204). In addition, the method has the problem of significant degradation of catalyst activity and of low space time yield, which is similar to the problem in the case of synthesis of phenol from benzoic acid.

The catalysts which were proposed by the inventors improved the above described problems and improved the conversion of benzoic acid and the selectivity to phenol. Nevertheless, the development of catalysts which further improve the catalyst life and which are applicable to other reaction systems such as the ones to obtain alkyl phenol such as cresol from alkyl benzoic acid at a high yield have been wanted.

5

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a catalyst which gives a high conversion of benzoic acid and alkyl benzoic acid and a high selectivity to phenol and alkyl phenol for a long period with a high space time yield, and to provide a method for producing phenol and alkyl phenol using the catalyst.

The present invention provides a catalyst for producing phenols consisting essentially of;

an iron oxide;

a nickel oxide;

at least one first oxide selected from the group consisting of a vanadium oxide and a molybdenum oxide; and

at least one second oxide selected from the group consisting of an alkali metal oxide and an alkaline earth metal oxide.

Further, the present invention provides a method for producing phenols using a catalyst from a benzoic acid or an alkyl benzoic acid, the catalyst consisting essentially of;

an iron oxide;

a nickel oxide;

at least one first oxide selected from the group consisting of a vanadium oxide and a molybdenum oxide; and

at least one second oxide selected from the group consisting of an alkali metal oxide and an alkaline earth metal oxide.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The ratio of nickel oxide to iron oxide ($\text{NiO}/\text{Fe}_2\text{O}_3$) in the catalyst is preferably in an approximate range of from 0.1 to 10.0 by weight, and most preferably from 0.3 to 5. When the ratio exceeds approximately 10.0 by weight, the yield of CO and CO_2 generated by complete combustion increases, and the selectivity to phenol or alkyl phenol decreases. When the ratio is lower than approximately 0.1, the yield of benzene or alkyl benzene becomes predominant, and the selectivity to phenol or alkyl phenol decreases.

The vanadium oxide is preferably vanadium pentoxide (V_2O_5), and may include vanadium monoxide (VO), vanadium trioxide (V_2O_3) and/or di-vanadium tetroxide (V_2O_4).

A preferable range of vanadium oxide content is approximately from 0.1 to 10wt.%, most preferably from 0.5 to 5wt.%. When the content of vanadium oxide is less than 0.1wt.%, the selectivity to phenol or alkyl phenol significantly degrades with time. When the content of vanadium oxide is above 10wt.%, the yield of CO and CO_2 generated by complete combustion increases.

The molybdenum oxide is preferably molybdenum trioxide (MoO_3), and may include molybdenum dioxide (MnO_2).

A preferable range of molybdenum oxide content is from 0.1 to 10wt.%, most preferably from 0.5 to 5wt.%. When the content of molybdenum oxide is less than 0.1wt.%, the selectivity to phenol or alkyl phenol significantly degrades with time. When the content of molybdenum oxide is above 10wt.%, the yield of CO and CO_2 generated by complete combustion increases.

Presence of either one of the vanadium oxide or the molybdenum oxide is sufficient, and the sum of the content of these two oxides in a range of from 0.1 to 10wt.% offers a satisfactory catalyst performance. Most preferable range of content of the sum of these oxides is from 0.5 to 5wt.%. When the content of the sum of these oxides is less than 0.1wt.%, the selectivity to phenol or alkyl phenol significantly degrades with time. When the content is above 10wt.%, the yield of CO and CO_2 generated by complete combustion increases.

Alkali metal oxide includes Li_2O , Na_2O , K_2O , Rb_2O , Cs_2O . Among them, the oxides of sodium and potassium are preferred because they yield less CO and CO_2 and give high conversion of benzoic acid and alkyl benzoic acid.

A preferable range of alkali metal oxide content is approximately from 0.05 to 30wt.%, most preferably from 0.05 to 10wt.%. When the content of alkali metal oxide is less than 0.05wt.%, the yield of CO and CO_2 increases and the selectivity to phenol or alkyl phenol significantly degrades. When the content of alkali metal oxide is above 10wt.%, the conversion of benzoic acid and alkyl benzoic acid degrades.

Alkaline earth metal oxides include MgO, CaO, SrO, BaO. Among them, the oxides of calcium are preferred because they yield less benzene and alkyl benzene and give higher conversion of benzoic acid and alkyl benzoic acid.

A preferable range of alkaline earth metal oxide content is approximately from 0.05 to 30wt.%, most preferably from 0.05 to 10wt.%. When the content of alkaline earth metal oxide is less than approximately 0.05wt.%, the yield of CO and CO₂ increases and the selectivity to phenol or alkyl phenol degrades. When the content of alkaline earth metal oxide is above 30wt.%, the conversion of benzoic acid and alkyl benzoic acid degrades, and the yield of benzene and alkyl benzene increases, and the selectivity to phenol and alkyl phenol degrades.

Presence of either one of the alkaline metal oxide or the alkali earth metal oxide is sufficient, or of both of them may be acceptable. The sum of the content of these two oxides in a range of from 0.05 to 30wt.% is sufficient.

The catalyst of the present invention may contain various compounds, and it may be supported on a titanium oxide or silica support.

The preparation of the catalyst of the present invention may be carried out using a known method applied for that type of catalysts. For example, the applicable raw materials include the nitrate, carbonate, organic salt, halide, hydroxide, and oxide of iron, nickel, vanadium or molybdenum, and alkali metal or alkaline earth metal. The method for mixing the above-described compounds of iron, nickel, vanadium or molybdenum, and alkali metal or alkaline earth metal may be conducted by a known process of precipitation, kneading, or impregnation. For instance, a prepared gel mixture of iron hydroxide and nickel hydroxide is mixed with the compounds of vanadium or molybdenum, and alkali metal or alkaline earth metal, or mixed with their solution, followed by drying and calcining. Otherwise, the kneaded product of iron oxide and nickel oxide may be mixed with the compounds of vanadium or molybdenum, and alkali metal or alkaline earth metal. The mixed and calcined product of iron oxide and nickel oxide may be mixed with the compounds of vanadium or molybdenum, and alkali metal or alkaline earth metal. The mixed and calcined product of iron oxide and nickel oxide may be impregnated with the compound of vanadium or molybdenum, and alkali metal or alkaline earth metal. The iron oxide, nickel oxide, vanadium oxide or molybdenum oxide, and oxide of alkali metal or alkaline earth metal may be powdered to mix, followed by compression molding to form pellets.

The catalyst is preferably calcined in air or inert gas during the preparation stage after the mixing of iron oxide and nickel oxide and is crystallized to one or more of iron oxide, nickel oxide, and composite oxide of iron and nickel. Generally, when a catalyst prepared by a known method is further calcined at a temperature of approximately 600 °C or more, the specific surface area reduces and the catalyst activity degrades. However, within a temperature range of from approximately 600 to 900 °C, the catalyst of the present invention reduces the specific surface area with the increase of calcining temperature, but the activity for yielding phenol and alkyl phenol increases, and gives a high conversion of benzoic acid and alkyl benzoic acid and a high selectivity to phenol and alkyl phenol. When the calcining temperature is lower than approximately 600 °C, only the reaction to yield CO and CO₂ by complete combustion proceeds while generating very little phenol and alkyl phenol, and induces the deposition of carbon materials on the catalyst surface. When the calcining temperature exceeds approximately 900 °C, the conversion of benzoic acid and alkyl benzoic acid becomes significantly low, and gives very slight amount of phenol and alkyl phenol generation.

The following is the method for producing phenol and alkyl phenol of the present invention.

The raw material is benzoic acid or mono-alkyl benzoic acid. The position of alkyl group substitution on monoalkyl benzoic acid may be either one of ortho-, meta-, or para-position. The alkyl group preferably has 1 to 8 carbons, more preferably 1 to 5, and most preferably around 1 to 3. Examples of the substituted benzoic acid are toluic acid, ethyl benzoic acid, and isopropylbenzoic acid.

According to the method of the present invention, oxygen is supplied along with the raw material benzoic acid or alkyl benzoic acid. The amount of oxygen may be at a theoretical quantity or more to the raw material benzoic acid or alkyl benzoic acid, and preferably in a range of from approximately 0.5 to 50 mole fold to the quantity of raw material. When the supply of oxygen exceeds approximately 50 mole fold, the complete oxidation of the raw material benzoic acid or alkyl benzoic acid is likely to occur. When the supply of oxygen is less than approximately 0.5 mole fold, sufficient conversion of benzoic acid or alkyl benzoic acid can not be attained.

The supplied oxygen may be in a form of molecular oxygen. Generally, however, air is used. The air may be diluted with an inert gas.

The reaction is usually conducted under the presence of water vapor. The water vapor supply is preferably in a range of from approximately 1 to 100 mole fold to the quantity of raw material benzoic acid

or alkyl benzoic acid. When the supply of water vapor exceeds approximately 100 mol fold, the operation becomes uneconomical. When the supply of water vapor is less than approximately 1 mol fold, generally the selectivity of phenol and alkyl phenol decreases.

A preferable range of space velocity is in a range of from approximately 100 to 50000 hr⁻¹. When the space velocity is less than approximately 100 hr⁻¹, sufficient space time yield can not be obtained. When the space velocity exceeds approximately 50000 hr⁻¹ the conversion of benzoic acid and alkyl benzoic acid decreases.

A preferable range of reaction temperature is approximately from 200 to 600 °C, most preferably from approximately 300 to 500 °C. When the reaction temperature is above approximately 600 °C, the selectivity of phenol and alkyl phenol decreases. When the reaction temperature is below approximately 200 °C, the conversion of benzoic acid and alkyl benzoic acid decreases.

The reaction pressure is not specifically limited if only the supplied raw material maintains gaseous phase under the reaction condition. Nevertheless, the reaction pressure is at atmospheric pressure or at a slightly positive pressure.

The method of the present invention may use either one of the fixed bed unit or the fluidized bed unit.

EXAMPLE

Example 1

Iron nitrate (Fe(NO₃)₃ • 9H₂O) 200g and nickel nitrate (Ni(NO₃)₂ • 6H₂O) 144g were dissolved to ion exchanged water 500ml. Sodium hydroxide of approximately 100g was dissolved to ion exchanged water 500ml. Both solutions were added dropwise to an ion exchanged water 2 liter at room temperature while maintaining the pH in a range of from 7 to 8. After completing the dropwise addition, the resulted solution was agitated for approximately 1 hr. The generated precipitate was filtered and washed.

The obtained gel was mixed with aqueous solution 100ml containing sodium carbonate (Na₂CO₃ • 10H₂O) 2.24g, and the mixture was agitated for approximately 1 hr. The gel was dried in air at 120 °C for 24 hrs., followed by calcining in air at 800 °C for 4 hrs.

The calcined product was put into an aqueous solution prepared by dissolving ammonium methavanadate (NH₄VO₃) 2g and oxalic acid ((COOH)₂) 4g. The mixture was evaporated to dry, followed by drying at 120 °C for 24 hrs. and calcining at 500 °C for 3 hrs. to obtain the catalyst.

The catalyst had the composition of Fe₂O₃:NiO:Na₂O:V₂O₅ = 50.3:47.1:0.6:2.0 (by weight).

Examples 2 - 8

Catalysts containing several levels of vanadium oxide content were prepared by the same procedure with that in Example 1. The obtained catalysts were used in Examples 111 to 117, and the compositions are listed in Tables 7 and 8.

Examples 9 - 15

Catalysts containing several levels of sodium oxide content were prepared by the same procedure with that in Example 1. The obtained catalysts were used in Examples 118 to 124, and the compositions are listed in Tables 9 and 10.

Examples 16 - 20

Catalysts containing several levels of vanadium oxide content and sodium oxide content were prepared by the same procedure with that in Example 1. The obtained catalysts were used in Examples 125 to 129, and the compositions are listed in Table 11.

Examples 21 - 26

Catalysts containing several levels of composition ratio of Fe₂O₃ to NiO were prepared by the same procedure with that in Example 1. The obtained catalysts were used in Examples 130 to 135, and the compositions are listed in Tables 12 and 13.

Examp l s 27 - 31

Catalysts w r pr pared by th same procedure with that in Exampl 1 xcept for varying the calcining t mperatur of $\text{Fe}_2\text{O}_3\text{-NiO-Na}_2\text{O}$ before supporting the vanadium component. Th obtained catalysts wer
5 used in Examples 136 to 140, and the compositions are listed in Table 14.

Example 32

Iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) 200g and nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) 144g were dissolved to ion
10 exchanged water 500ml. Sodium hydroxide of approximately 100g was dissolved to ion exchanged water 500ml. Both solutions were added dropwise to an ion exchanged water 2 liter at room temperature while maintaining the pH in a range of from 7 to 8. After completing the dropwise addition, the solution was agitated for approximately 1 hr. The generated precipitate was filtered and washed.

The obtained gel was mixed with aqueous solution 100ml containing sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) 3.68g, and the mixture was agitated for approximately 1 hr. The gel was dried in air at 120°C for
15 24 hrs., followed by calcining in air at 800°C for 4 hrs.

The calcined product was put into an aqueous solution prepared by dissolving ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) 2.93g. The mixture was evaporated to dry, followed by drying at 120°C for 24 hrs. and calcining at 500°C for 3 hrs. to obtain the catalyst.

20 The catalyst had the composition of $\text{Fe}_2\text{O}_3\text{:NiO:Na}_2\text{O:MoO}_3 = 49.6:46.4:1.0:3.0$ (by weight).

Examples 33 - 38

Catalysts containing several levels of molybdenum oxide content were prepared by the same procedure
25 with that in Example 32. The obtained catalysts were used in Examples 141 to 147, and the compositions are listed in Tables 15 and 16.

Examples 39 - 45

Catalysts containing several levels of sodium oxide content were prepared by the same procedure with
30 that in Example 32. The obtained catalysts were used in Examples 148 to 154, and the compositions are listed in Tables 17 and 18.

Examples 46 - 50

Catalysts containing several levels of molybdenum oxide content and sodium oxide content were
35 prepared by the same procedure with that in Example 32. The obtained catalysts were used in Examples 155 to 159, and the compositions are listed in Table 19.

40 Examples 51 - 56

Catalysts containing several levels of composition ratio of Fe_2O_3 to NiO were prepared by the same
procedure with that in Example 32. The obtained catalysts were used in Examples 160 to 165, and the
45 compositions are listed in Tables 20 and 21.

Examples 57 - 61

Catalysts were prepared by the same procedure with that in Example 32 except for varying the
50 calcining temperature of $\text{Fe}_2\text{O}_3\text{-NiO-Na}_2\text{O}$ before supporting the molybdenum component. The obtained catalysts were used in Examples 166 to 170, and the compositions are listed in Table 22.

Example 62

Iron nitrat ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) 200g and nick l nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) 144g wer dissolved to ion
55 xchanged wat r 500ml. Sodium hydroxide of approximately 100g was dissolved to ion xchanged wat r 500ml. Both solutions were added dropwise to an ion exchanged water 2 liter at room temperature while maintaining th pH in a rang of from 7 t 8. Aft r compl ting th dropwise addition, th solution was agitated for approximately 1 hr. Th g n rated pr cipitat was filt red and washed.

The obtained gel was mixed with aqueous solution 100ml containing sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) 3.70g, and the mixture was agitated for approximately 1 hr. The gel was dried in air at 120°C for 24 hrs., followed by calcining in air at 800°C for 4 hrs.

The calcined product was put into an aqueous solution 25ml prepared by dissolving ammonium methavanadate (NH_4VO_3) 2.06g and oxalic acid ($(\text{COOH})_2$) 4g and an aqueous solution 25ml prepared by dissolving ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) 1.47g. The mixture was evaporated to dry, followed by drying at 120°C for 24 hrs. and calcining at 500°C for 3 hrs. to obtain the catalyst.

The catalyst had the composition of $\text{Fe}_2\text{O}_3:\text{NiO}:\text{Na}_2\text{O}:\text{V}_2\text{O}_5:\text{MoO}_3 = 49.3:46.2:1.0:2.0:1.5$ (by weight).

10 Examples 63 - 71

Catalysts containing several levels of vanadium oxide content and molybdenum oxide content were prepared by the same procedure with that in Example 69. The obtained catalysts were used in Examples 172 to 180, and the compositions are listed in Tables 23 to 25.

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Example 72

Catalyst containing potassium carbonate (K_2CO_3) 0.71g instead of sodium carbonate 2.24g was prepared by the same procedure with that in Example 1. The obtained catalyst was used in Example 181, and the composition is listed in Table 26.

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Example 73

Catalyst containing lithium carbonate (Li_2CO_3) 1.20g instead of sodium carbonate 2.24g was prepared by the same procedure with that in Example 1. The obtained catalyst was used in Example 182, and the composition is listed in Table 26.

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Example 74

Catalyst containing rubidium carbonate (Rb_2CO_3) 0.60g instead of sodium carbonate 2.24g was prepared by the same procedure with that in Example 1. The obtained catalyst was used in Example 183, and the composition is listed in Table 26.

30

Example 75

35

Catalyst containing cesium carbonate (Cs_2CO_3) 0.56g instead of sodium carbonate 2.24g was prepared by the same procedure with that in Example 1. The obtained catalyst was used in Example 184, and the composition is listed in Table 26.

40 Example 76

Iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) 200g and nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) 144g were dissolved to ion exchanged water 500ml. Sodium hydroxide of approximately 100g was dissolved to ion exchanged water 500ml. Both solutions were added dropwise to an ion exchanged water 2 liter at room temperature while maintaining the pH in a range of from 7 to 8. After completing the dropwise addition, the solution was agitated for approximately 1 hr. The generated precipitate was filtered and washed.

45

The obtained gel was mixed with aqueous solution 100ml containing sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) 3.70g, and with aqueous solution 25ml prepared by dissolving ammonium methavanadate (NH_4VO_3) 2.06g and oxalic acid ($(\text{COOH})_2$) 4g, and with aqueous solution 25ml prepared by dissolving ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) 1.47g. The mixture was agitated for approximately 1 hr. to obtain a gel. The gel was dried in air at 120°C for 24 hrs., followed by calcining in air at 800°C for 4 hrs. to obtain the catalyst.

50

The catalyst had the composition of $\text{Fe}_2\text{O}_3:\text{NiO}:\text{Na}_2\text{O}:\text{V}_2\text{O}_5:\text{MoO}_3 = 49.3:46.2:1.0:2.0:1.5$ (by weight).

55 Example 77

Iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) 200g and nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) 144g were dissolved to ion exchanged water 500ml. Sodium hydroxide of approximately 100g was dissolved to ion exchanged water

500ml. Both solutions were added dropwise to an ion exchanged water 2 liter at room temperature while maintaining the pH in a range of from 7 to 8. After completing the dropwise addition, the solution was agitated for approximately 1 hr. The generated precipitate was filtered and washed.

The obtained gel was mixed with aqueous solution 100ml containing sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) 3.70g. The mixture was agitated for approximately 1 hr. The gel was dried in air at 120°C for 24 hrs., followed by calcining in air at 800°C for 4 hrs.

The calcined product was powdered, and was mixed with a vanadium pentoxide powder (V_2O_5) 1.55g. The mixture was compressed to form into cylindrical catalyst having the radius of 1mm and the length of 5mm.

The catalyst had the composition of $\text{Fe}_2\text{O}_3:\text{NiO}:\text{Na}_2\text{O}:\text{V}_2\text{O}_5 = 50.3:47.1:0.6:2.0$ (by weight).

Example 78

Iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) 200g and nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) 144g were dissolved to ion exchanged water 500ml. Sodium hydroxide of approximately 100g was dissolved to ion exchanged water 500ml. Both solutions were added dropwise to an ion exchanged water 2 liter at room temperature while maintaining the pH in a range of from 7 to 8. After completing the dropwise addition, the solution was agitated for approximately 1 hr. The generated precipitate was filtered and washed.

The obtained gel was dried in air at 120°C for 24 hrs., followed by calcining in air at 800°C for 4 hrs.

The fired product was put into an aqueous solution 100ml containing sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) 2.24g. and an aqueous solution 50ml prepared by dissolving ammonium metavanadate (NH_4VO_3) 2g and oxalic acid ($(\text{COOH})_2$) 4g. The mixture was evaporated to dry, followed by drying at 120°C for 24 hrs. and calcining at 500°C for 3 hrs. to obtain the catalyst. The catalyst had the composition of $\text{Fe}_2\text{O}_3:\text{NiO}:\text{Na}_2\text{O}:\text{V}_2\text{O}_5 = 50.3:47.1:0.6:2.0$ (by weight).

Example 79

Powders of hydroxyl-iron oxide ($\text{FeO}(\text{OH})$) 43.98g, nickel hydroxide ($\text{Ni}(\text{OH})_2$) 45.9g, sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) 3.70g, and vanadium pentoxide (V_2O_5) 1.55g were mixed together. The mixture was calcined in air at 800°C for 4 hrs. The calcined product was compressed to form into cylindrical catalyst having the radius of 1mm and the length of 5mm. The catalyst had the composition of $\text{Fe}_2\text{O}_3:\text{NiO}:\text{Na}_2\text{O}:\text{V}_2\text{O}_5 = 50.3:47.1:0.6:2.0$ (by weight).

Example 80

Catalyst containing magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) 3.09g instead of sodium carbonate 2.24g was prepared by the same procedure with that in Example 1. The obtained catalyst was used in Example 189, and the composition is listed in Table 28.

Example 81

Catalyst containing calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) 2.04g instead of sodium carbonate 2.24g was prepared by the same procedure with that in Example 1. The obtained catalyst was used in Example 190, and the composition is listed in Table 28.

Example 82

Catalyst containing strontium nitrate ($\text{Sr}(\text{NO}_3)_2$) 0.99g instead of sodium carbonate 2.24g was prepared by the same procedure with that in Example 1. The obtained catalyst was used in Example 191, and the composition is listed in Table 28.

Example 83

Catalyst containing barium nitrate ($\text{Ba}(\text{NO}_3)_2$) 0.83g instead of sodium carbonate 2.24g was prepared by the same procedure with that in Example 1. The obtained catalyst was used in Example 192, and the composition is listed in Table 28.

Exempl 84

Catalyst containing magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) 5.08g instead of sodium carbonate 3.68g was prepared by the same procedure with that in Example 32. The obtained catalyst was used in Example 193, and the composition is listed in Table 29.

Example 85

Catalyst containing calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) 3.35g instead of sodium carbonate 3.68g was prepared by the same procedure with that in Example 32. The obtained catalyst was used in Example 194, and the composition is listed in Table 29.

Example 86

Catalyst containing barium nitrate ($\text{Ba}(\text{NO}_3)_2$) 1.36g instead of sodium carbonate 3.68g was prepared by the same procedure with that in Example 32. The obtained catalyst was used in Example 195, and the composition is listed in Table 29.

Comparative Example 1

A catalyst was prepared by the same procedure with that in Example 1 except for not using ammonium methavanadate and oxalic acid.

Comparative Example 2

A catalyst was prepared in accordance with the Example 1 described in JP-B-64-934. A γ -alumina 30g was dipped into a solution of ion exchanged water 80g containing ammonium molybdate 1.73g, ammonium methavanadate 1.72g, copper nitrate 4.14g, 28% aqueous ammonia 75g, and monoethanol amine 4g. After heating the mixture at 80 °C for 10 min., the mixture was evaporated to dry in an evaporator under a reduced pressure for 1 hr., followed by calcining at 750 °C for 3 hrs. The obtained catalyst was dipped into an ion exchanged water 20g containing sodium hydroxide 2.74g. Then the catalyst was evaporated to dry in an evaporator, followed by calcining at 600 °C for 8 hrs.

Comparative Example 3

A catalyst was prepared in accordance with the Example 1 described in JP-B-59-20384. Copper sulfate 120g and zirconium oxynitrate 18g were dissolved to ion exchanged water 30g. The mixture was heated to 70 to 80 °C. An α -alumina 100g was dipped into the solution. The solution was dried, and calcined at 750 °C for 2 hrs. The catalyst was dipped into an ion exchanged water 30g containing potassium hydroxide 4.3g, followed by drying and by calcining at 500 °C for 16 hrs.

II. Reaction method

Each catalyst was pulverized to a specified size, which was then filled into a quartz tube having an inside diameter of 20mm. to a specified quantity. A predetermined amount of benzoic acid, steam, and air were introduced to the tube to react them at a specified temperature.

III. Condition and result of reaction

Examples 87 - 90

The catalyst of Example 1 was used under various reaction temperature levels. The condition and result of the reaction are summarized in Table 1.

Examples 91 - 98

The catalyst of Example 1 was used under various Space Velocity. The condition and result of the reaction are summarized in Tables 2 and 3.

Examples 99 - 102

The catalyst of Example 1 was used under various air concentrations. The condition and result of the reaction are summarized in Table 4.

Examples 103 - 106

The catalyst of Example 1 was used under various steam quantities. The condition and result of the reaction are summarized in Table 5.

Examples 107 - 110

The catalyst of Example 1 was used under various raw materials. The condition and result of the reaction are summarized in Table 6.

Examples 111 - 114

Catalysts of Examples 2 through 5 were used. The condition and result of reaction are summarized in Table 7.

Examples 115 - 117

Catalysts of Examples 6 through 8 were used. The condition and result of reaction are summarized in Table 8.

Examples 118 - 121

Catalysts of Examples 9 through 12 were used. The condition and result of reaction are summarized in Table 9.

Examples 122 - 124

Catalysts of Examples 13 through 15 were used. The condition and result of reaction are summarized in Table 10.

Examples 125 - 129

Catalysts of Examples 16 through 20 were used. The condition and result of reaction are summarized in Table 11.

Examples 130 - 133

Catalysts of Examples 21 through 24 were used. The condition and result of reaction are summarized in Table 12.

Examples 134 - 135

Catalysts of Examples 25 and 26 were used. The condition and result of reaction are summarized in Table 13.

Examples 136 - 140

Catalysts of Examples 27 through 31 were used. The condition and result of reaction are summarized in Table 14.

Examples 141 - 144

Catalysts of Examples 32 through 35 were used. The condition and result of reaction are summarized in Table 15.

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Examples 145 - 147

Catalysts of Examples 36 through 38 were used. The condition and result of reaction are summarized in Table 16.

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Examples 148 - 151

Catalysts of Examples 39 through 42 were used. The condition and result of reaction are summarized in Table 17.

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Examples 152 - 154

Catalysts of Examples 43 through 45 were used. The condition and result of reaction are summarized in Table 18.

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Examples 155 - 159

Catalysts of Examples 46 through 50 were used. The condition and result of reaction are summarized in Table 19.

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Examples 160 - 163

Catalysts of Examples 51 through 54 were used. The condition and result of reaction are summarized in Table 20.

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Examples 164 - 165

Catalysts of Examples 55 and 56 were used. The condition and result of reaction are summarized in Table 21.

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Examples 166 - 170

Catalysts of Examples 57 through 61 were used. The condition and result of reaction are summarized in Table 22.

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Examples 171 - 174

Catalysts of Examples 62 through 65 were used. The condition and result of reaction are summarized in Table 23.

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Examples 175 - 178

Catalysts of Examples 66 through 69 were used. The condition and result of reaction are summarized in Table 24.

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Examples 179 - 180

Catalysts of Examples 70 and 71 were used. The condition and result of reaction are summarized in Table 25.

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Examples 181 - 184

Catalysts of Examples 72 through 75 were used. The condition and result of reaction are summarized in Table 26.

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Examples 185 - 188

Catalysts of Examples 76 through 79 were used. The condition and result of reaction are summarized in Table 27.

10

Examples 189 - 192

Catalysts of Examples 80 through 83 were used. The condition and result of reaction are summarized in Table 28.

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Examples 193 - 195

Catalysts of Examples 84 through 86 were used with o-toluic acid as the raw material. The condition and result of reaction are summarized in Table 29.

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Comparative Examples 4 - 6

Catalysts of Comparative Examples 1 through 3 were used. The condition and result of reaction are summarized in Table 30.

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Example 196 and Comparative Examples 7 and 8

Catalysts of Example 62, Comparative Examples 2 and 3 were used with o-toluic acid as the raw material. The condition and result of reaction are summarized in Table 31.

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Table 1

			Example 87	Example 88	Example 89	Example 90
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)
	Calcining temperature (°C)*		800	800	800	800
	Use quantity (ml)		5.5	5.5	5.5	5.5
Reaction condition	Reaction Temperature (°C)		420	400	300	500
	Feed gas concentration (%)	Benzoic acid	3.8	3.8	3.8	3.8
		Water vapor	76.9	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4	15.4
	Space velocity (h ⁻¹)		2150	3400	3400	3400
Time after the start of reaction (h)		110	110	110	110	
Reaction result	Conversion of benzoic acid (%)		93.7	90.5	27.5	100.0
	Selectivity**	Phenol	91.0	90.9	95.9	84.3
		Benzene	4.7	8.1	3.6	15.2
		CO,CO ₂	4.3	0.8	0.3	0.4
	Space time yield of phenol (g/l·h)		292	446	143	457

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Table 2

			Example 91	Example 92	Example 93	Example 94
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)
	Calcining temperature (°C)*		800	800	800	800
	Use quantity (ml)		5.5	5.5	5.5	5.5
Reaction condition	Reaction Temperature (°C)		420	420	420	420
	Feed gas concentration (%)	Benzoic acid	3.8	3.8	3.8	3.8
		Water vapor	76.9	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4	15.4
	Space velocity (h ⁻¹)		1250	3800	5500	8020
Time after the start of reaction (h)			110	110	110	110
Reaction result	Conversion of benzoic acid (%)		100.0	90.0	87.5	85.0
	Selectivity**	Phenol	94.0	90.1	91.9	90.3
		Benzene	2.5	8.4	7.6	8.2
		CO,CO ₂	3.3	0.8	0.2	1.4
	Space time yield of phenol (g/l·h)		187	496	705	982

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Table 3

			Example 95	Example 96	Example 97	Example 98
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)
	Calcining temperature (°C)*		800	800	800	800
	Use quantity (ml)		5.5	5.5	5.5	5.5
Reaction condition	Reaction Temperature (°C)		420	420	420	420
	Feed gas concentration (%)	Benzoic acid	3.8	3.8	3.8	3.8
		Water vapor	76.9	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4	15.4
	Space velocity (h ⁻¹)		9500	15000	18000	21000
Time after the start of reaction (h)			110	110	110	110
Reaction result	Conversion of benzoic acid (%)		76.9	50.6	47.3	27.4
	Selectivity**	Phenol	91.0	90.4	90.5	92.3
		Benzene	5.7	7.2	8.5	7.2
		CO,CO ₂	3.3	1.8	0.3	0.5
	Space time yield of phenol (g/l·h)		1060	1094	1229	847

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Table 4

5				Example 99	Example 100	Example 101	Example 102
10	Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)
15		Calcining temperature (°C)*		800	800	800	800
20		Use quantity (ml)		5.5	5.5	5.5	5.5
25	Reaction condition	Reaction Temperature (°C)		420	420	420	420
30		Feed gas concentration (%)	Benzoic acid	3.8	3.8	3.8	0.6
35			Water vapor	76.9	76.9	76.9	11.7
			Oxygen	1.9	7.6	15.4	17.5
			Nitrogen	17.3	11.6	3.8	70.2
		Space velocity (h ⁻¹)		3400	3400	3400	3400
	Time after the start of reaction (h)			110	110	110	110
40	Reaction result	Conversion of benzoic acid (%)		69.7	99.8	100.0	100.0
45		Selectivity**	Phenol	92.0	85.3	85.9	80.2
			Benzene	3.7	10.1	10.6	16.2
			CO,CO ₂	3.3	4.5	3.5	3.6
		Space time yield of phenol (g/l · h)		348	461	466	69

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Table 5

			Example 103	Example 104	Example 105	Example 106
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)
	Calcining temperature (°C)*		800	800	800	800
	Use quantity (ml)		5.5	5.5	5.5	5.5
Reaction condition	Reaction Temperature (°C)		420	420	420	420
	Feed gas concentration (%)	Benzoic acid	9.1	6.3	2.8	1.8
		Water vapor	45.5	62.5	83.3	89.3
		Oxygen	9.1	6.3	2.8	1.8
		Nitrogen	36.3	24.9	11.1	7.1
	Space velocity (h ⁻¹)		1440	2090	4710	7320
Time after the start of reaction (h)		110	110	110	110	
Reaction result	Conversion of benzoic acid (%)		90.5	92.8	95.0	95.2
	Selectivity**	Phenol	85.8	88.4	93.1	93.0
		Benzene	8.7	7.1	3.2	3.4
		CO,CO ₂	3.2	2.5	3.5	3.6
	Space time yield of phenol (g/l·h)		427	453	489	490

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Table 6

			Example 107	Example 108	Example 109	Example 110
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)
	Calcining temperature (°C)*		800	800	800	800
	Use quantity (ml)		5.5	5.5	5.5	5.5
Reaction condition	Alkyl benzoic acid group as raw material		o-toluic acid	p-toluic acid	p-isopropyl benzoic acid	p-ethyl benzoic acid
	Reaction Temperature (°C)		420	420	420	420
	Feed gas concentration (%)	Alkyl benzoic acid	3.8	3.8	3.8	3.8
		Water vapor	76.9	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4	15.4
	Space velocity (h ⁻¹)		3400	3400	3400	3400
Time after the start of reaction (h)		110	110	110	110	
Reaction result	Conversion of raw material (%)		35.6	56.2	25.9	33.2
	Selectivity**	Alkyl phenol group	65.8 (m-cresol)	78.4 (m-cresol)	53.1 (m-isopropyl phenol)	33.0 (m-ethyl phenol)
		CO,CO ₂	11.2	12.2	22.1	24.1
	Space time yield of phenol (g/l·h)		146	275	108	77

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Table 7

			Example 111	Example 112	Example 113	Example 114
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (49.8:46.7 :0.6:3.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (49.2:44.8 :0.6:4.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (47.7:44.7 :0.6:7.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (46.1:43.3 :0.6:10.0)
	Calcining temperature (°C)*		800	800	800	800
	Use quantity (ml)		6.5	6.5	6.5	5.5
Reaction condition	Reaction Temperature (°C)		410	410	410	420
	Feed gas concentration (%)	Benzoic acid	3.2	3.2	3.1	3.8
		Water vapor	80.6	80.6	78.1	76.9
		Oxygen	3.2	3.2	3.1	3.8
		Nitrogen	12.9	12.9	12.5	15.4
	Space velocity (h ⁻¹)		3400	3400	3400	3400
Time after the start of reaction (h)			95	92	104	110
Reaction result	Conversion of benzoic acid (%)		90.6	87.5	87.1	83.7
	Selectivity**	Phenol	90.8	90.9	93.3	88.0
		Benzene	8.2	8.6	6.2	6.7
		CO,CO ₂	0.8	0.3	0.5	4.3
	Space time yield of phenol (g/l·h)		376	363	359	399

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Tabl 8

			Examl 115	Example 116	Example 117
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (49.8:46.7 :0.6:1.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (49.2:44.8 :0.6:0.5)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (47.7:44.7 :0.6:0.1)
	Calcining temperature (°C)*		800	800	800
	Use quantity (ml)		6.5	6.5	6.5
Reaction condition	Reaction Temperature (°C)		410	410	410
	Feed gas concentration (%)	Benzoic acid	3.8	3.8	3.8
		Water vapor	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4
	Space velocity (h ⁻¹)		3400	3400	3400
Time after the start of reaction (h)			110	110	110
Reaction result	Conversion of benzoic acid (%)		90.5	87.5	67.3
	Selectivity**	Phenol	88.8	81.2	80.3
		Benzene	10.2	14.6	15.2
		CO,CO ₂	0.8	3.3	4.5
	Space time yield of phenol(g/l·h)		436	385	293

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Table 9

			Example 118	Example 119	Example 120	Example 121
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.5:47.4 :0.05:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.5:47.3 :0.2:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.1:46.9 :1.0:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (46.5:46.5 :2.0:2.0)
	Calcining temperature (°C)*		800	800	800	800
	Use quantity (ml)		5.5	5.5	5.5	5.5
Reaction condition	Reaction Temperature (°C)		420	400	300	500
	Feed gas concentration (%)	Benzoic acid	3.8	3.8	3.8	3.8
		Water vapor	76.9	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4	15.4
	Space velocity (h ⁻¹)		3400	3400	3400	3400
Time after the start of reaction (h)		110	110	110	110	
Reaction result	Conversion of benzoic acid (%)		59.6	63.3	90.2	94.4
	Selectivity**	Phenol	90.0	90.8	92.3	91.0
		Benzene	6.3	7.2	5.4	5.3
		CO,CO ₂	2.9	1.8	2.3	2.9
	Space time yield of phenol (g/l·h)		291	312	451	466

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Tabl 10

			Examl 122	Examl 123	Examl 124
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (48.0:45.0 :5.0:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (45.4:41.1 :10.0:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (35.1:32.9 :30.0:2.0)
	Calcining temperature (° C)*		800	800	800
	Use quantity (ml)		5.5	5.5	5.5
Reaction condition	Reaction Temperature (° C)		420	400	300
	Feed gas concentration (%)	Benzoic acid	3.8	3.8	3.8
		Water vapor	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4
	Space velocity (h ⁻¹)		2150	3400	3400
Time after the start of reaction (h)			110	110	110
Reaction result	Conversion of benzoic acid (%)		93.4	66.3	47.5
	Selectivity**	Phenol	90.1	77.9	64.9
		Benzene	5.7	18.4	22.3
		CO,CO ₂	3.9	2.9	12.2
	Space time yield of phenol (g/l•h)		456	280	167

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Table 11

		Example 125	Example 126	Example 127	Example 128	Example 129
Catalyst	Composition (wt. ratio)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.0:46.9 :1.0:3.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (47.5:44.5 :2.0:6.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (45.4:42.6 :3.0:9.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (46.4:42.0 :0.05:10.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (36.1:33.8 :30.0:0.1)
	Calcining temperature (°C)*	800	800	800	800	800
	Use quantity (ml)	6.5	6.5	6.5	6.5	6.5
Reaction condition	Reaction Temperature (°C)	410	410	410	410	410
	Feed gas concentration (%)	Benzoic acid	3.1	3.1	3.2	3.2
		Water vapor	78.1	78.1	80.6	80.6
		Oxygen	3.1	3.1	3.2	3.2
		Nitrogen	12.5	12.5	12.9	12.9
	Space velocity (h ⁻¹)	3400	3400	3400	3400	3400
Time after the start of reaction (h)		104	101	93	110	110
Reaction result	Conversion of benzoic acid (%)	87.1	88.4	53.8	24.0	14.0
	Selectivity**	Phenol	93.3	92.1	88.0	52.5
		Benzene	6.2	6.6	8.1	0.8
		CO, CO ₂	0.5	1.1	3.8	3.6
	Space time yield of phenol (g/l·h)	359	360	216	105	34

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Table 12

			Example 130	Example 131	Example 132	Example 133
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ , (8.3:89.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ , (20.5:76.9 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ , (40.5:56.9 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ , (59.9:37.5 :0.6:2.0)
	Calcining temperature (°C)*		800	800	800	800
	Use quantity (ml)		5.5	5.5	5.5	5.5
Reaction condition	Reaction Temperature (°C)		420	420	420	420
	Feed gas concentration (%)	Benzoic acid	3.8	3.8	3.8	3.8
		Water vapor	76.9	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4	15.4
	Space velocity (h ⁻¹)		3400	3400	3400	3400
Time after the start of reaction (h)		110	110	110	110	
Reaction result	Conversion of benzoic acid (%)		43.6	70.5	87.5	95.0
	Selectivity**	Phenol	73.4	80.9	90.9	82.7
		Benzene	3.3	7.1	3.1	15.2
		CO,CO ₂	23.0	11.8	1.3	0.4
	Space time yield of phenol (g/l·h)		174	309	431	426

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Tabl 13

			Examl 134	Example 135
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (78.9:18.5 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (91.0:6.4 :0.6:2.0)
	Calcining temperature (° C)*		800	800
	Use quantity (ml)		5.5	5.5
Reaction condition	Reaction Temperature (° C)		420	420
	Feed gas concentration (%)	Benzoic acid	3.8	3.8
		Water vapor	76.9	76.9
		Oxygen	3.8	3.8
		Nitrogen	15.4	15.4
	Space velocity (h ⁻¹)		3400	3400
Time after the start of reaction (h)			110	110
Reaction result	Conversion of benzoic acid (%)		99.5	100.0
	Selectivity**	Phenol	71.0	60.2
		Benzene	22.9	38.1
		CO,CO ₂	4.2	0.7
	Space time yield of phenol (g/l•h)		383	326

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Table 14

			Example 136	Example 137	Example 138	Example 139	Example 140
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)
	Calcining temperature (°C)*		550	600	700	900	950
	Use quantity (ml)		5.5	5.5	5.5	5.5	5.5
Reaction condition	Reaction Temperature (°C)		420	420	420	420	420
	Feed gas concentration (%)	Benzoic acid	3.8	3.8	3.8	3.8	3.8
		Water vapor	76.9	76.9	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4	15.4	15.4
	Space velocity (h ⁻¹)		3400	3400	3400	3400	3400
Time after the start of reaction (h)		110	110	110	110	110	
Reaction result	Conversion of benzoic acid (%)		100.0	100.0	99.5	55.3	6.5
	Selectivity**	Phenol	33.1	60.3	70.5	91.2	74.6
		Benzene	25.3	20.3	13.5	2.3	14.3
		CO,CO ₂	40.3	16.5	12.3	6.5	11.1
	Space time yield of phenol (g/l·h)		179	327	380	273	26

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Table 15

			Example 141	Example 142	Example 143	Example 144
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (49.6:46.4 :1.0:3.0)	Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (51.0:47.9 :1.0:0.1)	Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (50.6:47.4 :1.0:1.0)	Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (50.1:46.9 :1.0:2.0)
	Calcining temperature (°C)*		800	800	800	800
	Use quantity (ml)		5.5	5.5	5.5	5.5
Reaction condition	Reaction Temperature (°C)		420	420	420	420
	Feed gas concentration (%)	Benzoic acid	3.8	3.8	3.8	3.8
		Water vapor	76.9	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4	15.4
	Space velocity (h ⁻¹)		2170	3400	3400	3400
Time after the start of reaction (h)			92	110	110	110
Reaction result	Conversion of benzoic acid (%)		60.1	70.5	60.2	62.3
	Selectivity**	Phenol	85.1	65.2	77.3	85.9
		Benzene	8.2	22.5	11.3	8.9
		CO,CO ₂	6.7	11.2	10.2	5.2
	Space time yield of phenol (g/l·h)		177	249	252	290

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Tabl 16

			Example 145	Exempl 146	Exempl 147
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (48.5:45.5 :1.0:5.0)	Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (47.0:44.0 :1.0:8.0)	Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (45.9:43.1 :1.0:10.0)
	Calcining temperature (°C)*		800	800	800
	Use quantity (ml)		5.5	5.5	5.5
Reaction condition	Reaction Temperature (°C)		420	420	420
	Feed gas concentration (%)	Benzoic acid	3.8	3.8	3.8
		Water vapor	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4
	Space velocity (h ⁻¹)		3400	3400	3400
Time after the start of reaction (h)			110	110	110
Reaction result	Conversion of benzoic acid (%)		65.4	59.2	53.6
	Selectivity**	Phenol	83.6	82.3	70.6
		Benzene	5.7	10.4	21.6
		CO,CO ₂	10.4	6.9	6.9
	Space time yield of phenol (g/l•h)		296	264	205

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Table 17

			Example 148	Example 149	Example 150	Example 151
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (50.0:46.9 :0.05:3.0)	Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (49.9:46.9 :0.2:3.0)	Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (49.7:46.7 :0.6:3.0)	Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (49.0:46.0 :2.0:3.0)
	Calcining temperature (°C)*		800	800	800	800
	Use quantity (ml)		5.5	5.5	5.5	5.5
Reaction condition	Reaction Temperature (°C)		420	420	420	420
	Feed gas concentration (%)	Benzoic acid	3.8	3.8	3.8	3.8
		Water vapor	76.9	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4	15.4
	Space velocity (h ⁻¹)		3400	3400	3400	3400
Time after the start of reaction (h)		110	110	110	110	
Reaction result	Conversion of benzoic acid (%)		33.5	42.1	65.8	67.5
	Selectivity**	Phenol	75.1	75.2	86.3	88.6
		Benzene	8.9	12.9	5.9	5.9
		CO,CO ₂	13.5	8.2	7.2	6.3
	Space time yield of phenol (g/l·h)		136	172	308	324

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Tabl 18

			Example 152	Example 153	Example 154
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (47.5:44.5 :5.0:3.0)	Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (44.9:42.1 :10.0:3.0)	Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (34.6:32.4 :30.0:3.0)
	Calcining temperature (°C)*		800	800	800
	Use quantity (ml)		5.5	5.5	5.5
Reaction condition	Reaction Temperature (°C)		410	410	410
	Feed gas concentration (%)	Benzoic acid	3.8	3.8	3.8
		Water vapor	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4
	Space velocity (h ⁻¹)		3400	3400	3400
Time after the start of reaction (h)			110	110	100
Reaction result	Conversion of benzoic acid (%)		63.5	52.3	36.9
	Selectivity**	Phenol	80.6	65.8	64.5
		Benzene	11.4	30.3	23.8
		CO,CO ₂	7.2	4.2	8.3
	Space time yield of phenol (g/l•h)		277	187	129

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Table 19

			Example 155	Example 156	Example 157	Example 158	Example 159
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (49.9:45.5 :0.6:4.0)	Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (47.5:44.5 :2.0:6.0)	Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (46.4:42.0 :0.05:10.0)	Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (36.1:33.8 :30.0:0.1)
	Calcining temperature (°C)*		800	800	800	800	800
	Use quantity (ml)		5.5	5.5	5.5	5.5	5.5
Reaction condition	Reaction Temperature (°C)		410	410	410	410	410
	Feed gas concentration (%)	Benzoic acid	3.8	3.2	3.1	3.8	3.8
		Water vapor	76.9	80.6	78.1	76.9	76.9
		Oxygen	3.8	3.2	3.1	3.8	3.8
		Nitrogen	15.4	12.9	12.5	15.4	15.4
	Space velocity (h ⁻¹)		2180	3400	3400	3400	3400
Time after the start of reaction (h)			95	100	93	110	110
Reaction result	Conversion of benzoic acid (%)		54.2	48.5	40.3	32.0	21.0
	Selectivity**	Phenol	87.8	88.1	86.3	61.2	50.2
		Benzene	7.9	7.5	8.1	19.5	40.3
		CO,CO ₂	4.3	4.4	5.6	18.5	6.5
	Space time yield of phenol (g/l·h)		165	195	154	106	57

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Table 20

			Example 160	Example 161	Example 162	Example 163
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (8.3:89.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (20.5:76.9 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (40.5:56.9 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (59.9:37.5 :0.6:2.0)
	Calcining temperature (°C)*		800	800	800	800
	Use quantity (ml)		5.5	5.5	5.5	5.5
Reaction condition	Reaction Temperature (°C)		420	420	420	420
	Feed gas concentration (%)	Benzoic acid	3.8	3.8	3.8	3.8
		Water vapor	76.9	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4	15.4
	Space velocity (hr ⁻¹)		3400	3400	3400	3400
Time after the start of reaction (h)		110	110	110	110	
Reaction result	Conversion of benzoic acid (%)		29.9	40.6	50.3	76.2
	Selectivity**	Phenol	80.3	86.2	89.6	83.2
		Benzene	2.9	7.6	3.1	10.3
		CO,CO ₂	11.5	5.9	5.6	6.3
	Space time yield of phenol (g/l·h)		130	190	244	343

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Tabl 21

			Example 164	Example 165
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (78.9:18.5 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-MoO ₃ (91.0:6.4 :0.6:2.0)
	Calcining temperature (° C)*		800	800
	Use quantity (ml)		5.5	5.5
Reaction condition	Reaction Temperature (° C)		420	420
	Feed gas concentration (%)	Benzoic acid	3.8	3.8
		Water vapor	76.9	76.9
		Oxygen	3.8	3.8
		Nitrogen	15.4	15.4
	Space velocity (h ⁻¹)		3400	3400
Time after the start of reaction (h)			110	110
Reaction result	Conversion of benzoic acid (%)		88.5	95.3
	Selectivity**	Phenol	74.2	55.3
		Benzene	12.9	22.3
		CO,CO ₂	10.3	20.9
	Space time yield of phenol (g/l•h)		356	286

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Table 22

Catalyst	Composition (wt. ratio)		Example 166	Example 167	Example 168	Example 169	Example 170
	Calcining temperature (°C)*		550	600	700	900	950
	Use quantity (ml)		5.5	5.5	5.5	5.5	5.5
Reaction condition	Reaction Temperature (°C)		420	420	420	420	420
	Feed gas concentration (%)	Benzoic acid	3.8	3.8	3.8	3.8	3.8
		Water vapor	76.9	76.9	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4	15.4	15.4
Reaction result	Space velocity (h ⁻¹)		3400	3400	3400	3400	3400
	Time after the start of reaction (h)		110	110	110	110	110
	Conversion of benzoic acid (%)		100.0	98.8	90.2	43.2	8.9
	Selectivity**	Phenol	61.2	62.1	70.9	86.5	72.1
		Benzene	15.6	13.3	8.5	6.3	14.0
		CO, CO ₂	22.3	16.4	21.5	3.5	11.1
Reaction result	Space time yield of phenol (g/l·h)		331	332	347	202	35

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Table 23

			Example 171	Example 172	Example 173	Example 174
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ -MoQ (49.3:46.2 1.0:2.0:1.5)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ -MoQ ₃ (47.5:44.5 1.0:4.0:3.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ -MoO ₃ (47.5:44.5 2.0:4.0:3.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ -MoO ₃ (50.1:46.9 2.0:0.5:0.5)
	Calcining temperature (°C)*		800	800	800	800
	Use quantity (ml)		5.5	5.5	5.5	5.5
Reaction condition	Reaction Temperature (°C)		420	420	420	420
	Feed gas concentration (%)	Benzoic acid	3.8	3.8	3.8	3.8
		Water vapor	76.9	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4	15.4
	Space velocity (h ⁻¹)		3400	3400	3400	3400
Time after the start of reaction (h)		110	110	110	110	
Reaction result	Conversion of benzoic acid (%)		83.9	88.9	95.3	62.5
	Selectivity**	Phenol	93.5	94.1	88.6	80.5
		Benzene	3.5	4.4	2.6	15.8
		CO,CO ₂	1.4	0.5	8.1	5.1
	Space time yield of phenol (g/l·h)		425	453	458	273

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Table 24

			Example 175	Example 176	Example 177	Example 178
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ -MoO ₃ (50.5:47.3 2.0:0.1:0.1)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ -MoO ₃ (45.4:42.6 2:5:5)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ -MoO ₃ (40.2:37.8 2:10:10)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ -MoO ₃ (25.8:24.2 30:10:10)
	Calcining temperature (°C)*		800	800	800	800
	Use quantity (ml)		5.5	5.5	5.5	5.5
Reaction condition	Reaction Temperature (°C)		420	420	420	420
	Feed gas concentration (%)	Benzoic acid	3.8	3.8	3.8	3.8
		Water vapor	76.9	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4	15.4
	Space velocity (h ⁻¹)		3400	3400	3400	3400
Time after the start of reaction (h)			110	110	110	110
Reaction result	Conversion of benzoic acid (%)		44.3	77.7	85.4	55.5
	Selectivity**	Phenol	71.5	84.3	89.8	51.0
		Benzene	21.1	8.4	3.3	15.4
		CO,CO ₂	5.9	5.6	5.0	31.8
	Space time yield of phenol (g/l·h)		172	355	416	153

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Tabl 25

			Example 179	Example 180
5	Catalyst	Composition (wt. ratio)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ -MoO ₃ (51.5:48.3 0.05:0.1:0.1)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ -MoO ₃ (45.4:42.6 1:10:1)
		Calcining temperature (°C)*	800	800
10		Use quantity (ml)	5.5	5.5
	Reaction condition	Reaction Temperature (°C)	420	420
15		Feed gas concentration (%)		
		Benzoic acid	3.8	3.8
		Water vapor	76.9	76.9
		Oxygen	3.8	3.8
20		Nitrogen	15.4	15.4
		Space velocity (h ⁻¹)	3400	3400
	Time after the start of reaction (h)		110	110
25	Reaction result	Conversion of benzoic acid (%)	35.1	55.9
		Selectivity**		
		Phenol	76.6	86.1
		Benzene	12.9	7.4
		CO,CO ₂	10.0	4.6
30		Space time yield of phenol (g/l•h)	146	261

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Table 26

			Example 181	Example 182	Example 183	Example 184
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -K ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Li ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Rb ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Cs ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)
	Calcining temperature (°C)*		800	800	800	800
	Use quantity (ml)		5.5	5.5	5.5	5.5
Reaction condition	Reaction Temperature (°C)		420	420	420	420
	Feed gas concentration (%)	Benzoic acid	3.8	3.8	3.8	3.8
		Water vapor	76.9	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4	15.4
	Space velocity (h ⁻¹)		3400	3400	3400	3400
Time after the start of reaction (h)		110	110	110	110	
Reaction result	Conversion of benzoic acid (%)		85.9	66.8	54.3	44.3
	Selectivity**	Phenol	90.6	90.1	83.6	70.6
		Benzene	5.4	3.3	7.5	16.3
		CO,CO ₂	2.3	6.4	8.5	10.3
	Space time yield of phenol (g/l·h)		422	326	246	170

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Table 27

		Example 185	Example 186	Example 187	Example 188
Catalyst	Composition (wt. ratio)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ -MoO ₃ (49.3:46.2 1.0:2.0:1.5)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ (50.3:47.1 :0.6:2.0)
	Use quantity (ml)	5.5	5.5	5.5	5.5
Reaction condition	Reaction Temperature (°C)		420	420	420
	Feed gas concentration (%)	Benzoic acid	3.8	3.8	3.8
		Water vapor	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4
	Space velocity (h ⁻¹)		3400	3400	3400
Time after the start of reaction (h)		110	110	110	110
Reaction result	Conversion of benzoic acid (%)		94.9	65.9	41.3
	Selectivity**	Phenol	93.2	96.3	98.0
		Benzene	5.3	1.2	1.0
		CO,CO ₂	1.1	1.3	0.6
	Space time yield of phenol (g/l·h)		480	344	219
					137

Table 28

			Example 189	Example 190	Example 191	Example 192
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -MgO-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -CaO-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -SrO-V ₂ O ₅ (50.3:47.1 :0.6:2.0)	Fe ₂ O ₃ -NiO -BaO-V ₂ O ₅ (50.3:47.1 :0.6:2.0)
	Calcining temperature (°C)*		800	800	800	800
	Use quantity (ml)		5.5	5.5	5.5	5.5
Reaction condition	Reaction Temperature (°C)		420	400	300	500
	Feed gas concentration (%)	Benzoic acid	3.8	3.8	3.8	3.8
		Water vapor	76.9	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4	15.4
	Space velocity (h ⁻¹)		2150	3400	3400	3400
Time after the start of reaction (h)		110	110	110	110	
Reaction result	Conversion of benzoic acid (%)		63.5	55.3	43.2	50.3
	Selectivity**	Phenol	90.3	90.4	89.3	88.8
		Benzene	2.3	5.1	1.5	10.2
		CO,CO ₂	7.3	3.8	8.1	1.3
	Space time yield of phenol (g/l·h)		196	271	209	242

* Calcining temperature of Fe₂O₃-NiO-Na₂O before supporting V₂O₅.

** C-mol%

Tabl 29

			Example 193	Exempl 194	Exempl 195
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO -MgO-MoO ₃ (49.6:46.4 :1.0:3.0)	Fe ₂ O-NiO -CaO-MoO ₃ (51.0:47.9 :1.0:0.1)	Fe ₂ O ₃ -NiO -BaO-MoO ₃ (50.6:47.4 :1.0:1.0)
	Use quantity (ml)		5.5	5.5	5.5
Reaction condition	Alkyl benzoic acid group as raw material		o-toluic acid	o-toluic acid	o-toluic acid
	Reaction Temperature (°C)		420	420	420
	Feed gas concentration (%)	Alkyl benzoic acid	3.8	3.8	3.8
		Water vapor	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4
	Space velocity (h ⁻¹)		3400	3400	3400
Time after the start of reaction (h)			110	110	110
Reaction result	Conversion of raw material (%)		59.6	42.5	40.3
	Selectivity**	Alkyl phenol group	70.2 (m-cresol)	66.6 (m-cresol)	72.2 (m-cresol)
		CO,CO ₂	11.6	13.5	10.2
	Space time yield of phenol (g/l•h)			261	177

** C-mol%

Tabl 30

			Comparative xample 4	Comparativ example 5	Comparativ example 6
Catalyst	Composition (wt. ratio)		Fe ₂ O ₃ -NiO-Na ₂ O (51.3:48.1:0.6)	MoO ₃ -V ₂ O ₅ -C- uO -Na ₂ O-Al ₂ O ₃ (3.9:3.7:3.8:5.- 9:82.7)	CuO-ZnO-K ₂ O- -Al ₂ O ₃ (4.0:3.0:3.6:89.- 4)
	Use quantity (ml)		6.5	5.9	5.3
Reaction condition	Reaction Temperature (°C)		410	300	300
	Feed gas concentration (%)	Benzoic acid	2.7	2.3	2.3
		Water vapor	69.4	69.9	69.9
		Oxygen	5.6	4.7	4.7
		Nitrogen	22.2	23.1	23.1
	Space velocity (h ⁻¹)		3950	2640	2960
Time after the start of reaction (h)			91	83	87
Reaction result	Conversion of benzoic acid (%)		31.2	35.6	12.2
	Selectivity [™]	Phenol	24.0	51.9	26.3
		Benzene	38.9	18.7	53.6
		CO,CO ₂	36.7	29.4	20.1
	Space time yield of phenol (g/l•h)		21	47	9

^{**} C-mol%

Tabl 31

5			Example 196	Comparativ example 7	Comparativ example 8
10	Catalyst	Composition (wt. ratio)	Fe ₂ O ₃ -NiO -Na ₂ O-V ₂ O ₅ -MoO ₃ (49.3:46.2 1.0:2.0:1.5)	MoO ₃ -V ₂ O ₅ -CuO -Na ₂ O-Al ₂ O ₃ (3.9:3.7:3.8 :5.9:82.7) :0.6:2.0)	CuO-ZnO-K ₂ O -Al ₂ O ₃ (4.0:3.0:3.6 :89.4) :0.6:2.0)
		Use quantity (ml)	5.5	5.5	5.5
15	Reaction condition	Alkyl benzoic acid group as raw material	o-toluic acid	o-toluic acid	o-toluic acid
		Reaction Temperature (°C)	420	300	300
		Feed gas concentration (%)	Alkyl benzoic acid	3.8	3.8
		Water vapor	76.9	76.9	76.9
		Oxygen	3.8	3.8	3.8
		Nitrogen	15.4	15.4	15.4
		Space velocity (h ⁻¹)	3400	3400	3400
	Time after the start of reaction (h)		110	110	110
	Reaction result	Conversion of raw material (%)	42.5	23.5	11.5
		Selectivity**	Alkyl phenol group	63.2	2.8
		CO,CO ₂	10.9	28.9	31.6
	Space time yield of phenol (g/l·h)		167	4	1

** C-mol%

Claims

1. A catalyst for producing phenols consisting essentially of;
 an iron oxide;
 a nickel oxide;
 at least one first oxide selected from the group consisting of a vanadium oxide and a molybdenum oxide; and
 at least one second oxide selected from the group consisting of an alkali metal oxide and an alkaline earth metal oxide.
2. The catalyst of claim 1, wherein said iron oxide and said nickel oxide have a ratio of NiO to Fe₂O₃ being from 0.1 to 10 by weight.
3. The catalyst of claim 2, wherein said ratio of NiO to Fe₂O₃ is from 0.3 to 5 by weight.
4. The catalyst of claim 1, wherein said at least one first oxide is a vanadium oxide.

5. The catalyst of claim 4, wherein vanadium oxide content is from 0.1 to 10 wt.%.
6. The catalyst of claim 5, wherein said vanadium oxide content is from 0.5 to 5 wt.%.
7. The catalyst of claim 4, wherein said vanadium oxide is vanadium pentoxide.
8. The catalyst of claim 1, wherein said at least one first oxide is a molybdenum oxide.
9. The catalyst of claim 8, wherein molybdenum oxide content is from 0.1 to 10 wt.%.
10. The catalyst of claim 9, wherein said molybdenum oxide content is from 0.5 to 5 wt.%.
11. The catalyst of claim 8, wherein said molybdenum oxide is a molybdenum trioxide.
12. The catalyst of claim 1, wherein said at least one first oxide is a vanadium oxide and a molybdenum oxide, and a sum of vanadium oxide content and molybdenum oxide content is from 0.1 to 10 wt.%.
13. The catalyst of claim 12, wherein said sum of vanadium oxide content and molybdenum oxide content is from 0.5 to 5 wt.%.
14. The catalyst of claim 1, wherein said at least one second oxide is an alkali metal oxide.
15. The catalyst of claim 14, wherein said alkali metal oxide is Li_2O , Na_2O , K_2O , Rb_2O or Cs_2O .
16. The catalyst of claim 15, wherein said alkali metal oxide is Na_2O or K_2O .
17. The catalyst of claim 14, wherein content of said alkali metal oxide is from 0.05 to 30 wt.%.
18. The catalyst of claim 17, wherein content of said alkali metal oxide is from 0.05 to 10 wt.%.
19. The catalyst of claim 1, wherein said at least one second oxide is an alkaline earth metal oxide.
20. The catalyst of claim 19, wherein said alkaline earth metal oxide is MgO , CaO , SrO or BaO .
21. The catalyst of claim 20, wherein said alkaline earth metal oxide is CaO .
22. The catalyst of claim 19, wherein content of said alkaline earth metal oxide is from 0.05 to 30 wt.%.
23. The catalyst of claim 19, wherein content of said alkaline earth metal oxide is from 0.05 to 10 wt.%.
24. The catalyst of claim 1, wherein said at least one second oxide is an alkali metal oxide and an alkaline earth metal oxide.
25. The catalyst of claim 24, wherein sum of alkali metal oxide content and alkaline earth metal oxide is from 0.05 to 30 wt.%.
26. A method for producing phenols using a catalyst from benzoic acid or an alkyl benzoic acid, the catalyst for producing phenols consisting essentially of:
 - a nickel oxide;
 - at least one first oxide selected from the group consisting of a vanadium oxide and a molybdenum oxide; and
 - at least one second oxide selected from the group consisting of an alkali metal oxide and an alkaline earth metal oxide.
27. The method of claim 26, which is conducted by reacting a benzoic acid or an alkyl benzoic acid with oxygen and water vapor.

28. The method of claim 27, wherein oxygen amount is from 0.5 to 50 mol fold to the benzoic acid or alkyl benzoic acid.
29. The method of claim 27, wherein water vapor amount is from 1 to 100 mol fold to the benzoic acid or alkyl benzoic acid.
30. The method of claim 27, wherein said alkyl benzoic acid has an alkyl group with 1 to 8 carbon atoms on ortho-, meta-, or para-position.
31. The method of claim 30, wherein said alkyl benzoic acid has an alkyl group with 1 to 5 carbon atoms on ortho-, meta-, or para-position.
32. The method of claim 27, wherein said reaction is performed at a space velocity of 100 to 50000 hr⁻¹.
33. The method of claim 27, wherein said reaction is performed at a temperature of 200 to 600 °C.
34. The method of claim 27, wherein said temperature is from 300 to 500 °C.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 11 2072

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DATABASE WPI Week 9246, Derwent Publications Ltd., London, GB; AN 92-378182 & JP-A-4 279 538 (NKK) * abstract *	1,26	C07C37/56 C07C39/04 B01J23/84 B01J23/88
D,X	EP-A-0 052 839 (SUMITOMO) * claims * & JP-B-1 000 934 (...)	1,26	
D,A	EP-A-0 538 912 (NKK) * claims; examples * & JP-A-4 005 250 (...)	1,26	
X	US-A-3 926 853 (M SENES ET LA) * claim 1 *	1	
X	EP-A-0 226 640 (NIPPON SHOKUBAI) * claim 1 *	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C07C B01J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21 October 1994	Examiner Heywood, C
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure F : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document	